THE INFLUENCE OF COAL SURFACE CHEMISTRY ON THE ADSORPTION OF COAL CONVERSION CATALYSTS

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INTRODUCTION

Prior to its gasification, coal is generally loaded with catalytic materials by mechanically mixing the coal with a solid catalyst precursor, by impregnation with a solution containing the catalyst precursor (incipient wetness technique), or by ion-exchange of the catalyst precursor metal ions with protons on the coal (1-3). For the same catalytic material, the various techniques typically produce different coal char reactivities under identical reaction conditions. The disparities in catalyst performance has been attributed to differences in catalyst dispersion, induced by differences in coal-catalyst contact.

Despite their significant influence on catalyst activity, the effects of interfacial phenomena on the adsorption of coal gasification metal catalysts has not been previously investigated. This paper describes the effects of coal surface charge on the adsorption of calcium and potassium ions from solution.

EXPERIMENTAL

The coals used in the study are a lignite (PSOC 1482) and a subbituminous coal (PSOC 1485), both of which were sealed in argon and supplied by the Penn State Coal Sample Bank. The ultimate and proximate analyses of the coals are provided in Table 1.

The surface charge properties of the coals were measured at room temperature using a Pen Kem Model 501 Lazer Zee Meter zeta potential instrument. Slurries were prepared by dispersing 300mg samples of each coal (equal proportions of -20 and -80 U.S. mesh sizes) in a liter of deionized water containing 10⁻³ moles 1⁻¹ AgNO₃ for ionic strength control. After the coal particles have been well-dispersed by

agitation in an ultrasonic bath, the sediments were separated from the suspended particles, the latter fraction was divided into 50.0 cm³ portions, and the pH's of the dispersions were varied with nitric acid or ammonium hydroxide solutions. After 4h equilibration (by mechanical agitation), each sample was transferred to the zetameter and the zeta potential of the coal particles were measured.

The effect of coal surface charge on the adsorption of potassium and calcium ions was determined by dispersing 1.0g samples of coal in 10^{-2} or 10^{-3} moles 1^{-1} of K^+ or Ca^{2+} . The samples were conditioned by shaking for 24h after which they were filtered and the filtrates analyzed for potassium or calcium with atomic absorption spectrophometry. Metals uptake were calculated as the difference in Ca or K content of the solutions prior to and after adsorption.

RESULTS AND DISCUSSION

The zeta potential results given in Figure 1 show that the surfaces of the lignite coal particles are negatively charged over a wide range of pH and that the isoelectric point (iep) occurs at about pH 1.9, the surfaces of the coal particles being positively and negatively charged, respectively, below and above this pH value. A review of the iep's of coals shows that the iep of coals occurs in the acidic range (4).

A striking feature of Figure 1 is that the negative charge density increases with increase in pH. A similar trend was observed for the subbituminous coal. These observations can be explained in terms of the surface functional groups on coal. It is well known that the surfaces of low-rank coals are dominated by oxygenated surface groups. Several studies [5-7] have shown that the surface chemistry of these coals is determined by these groups, although inorganic species also play a role [6]. In aqueous and basic environments, these acidic groups dissociate and the coal particles acquire negative charges, whereas the surface groups are protonated in acidic medium, reducing the negative charge density, and the surface may become positively charged in strongly acidic media [5,6]. The formation of surface charge on coals is depicted by equations (1)-(4) for carboxyl (COOH) and hydroxyl (OH) functional groups:

$$-\text{COOH}_{(s)} + \text{OH}^- \longrightarrow -\text{COO}_{(s)} + \text{H}_2\text{O}$$
 (1)
 $-\text{COH}_{(s)} + \text{OH}^- \longrightarrow -\text{CO}_{(s)} + \text{H}_2\text{O}$ (2)

$$-COOH_{(s)} + H^{+} - - - -COOH_{2}^{+}_{(s)}$$
 (3)

$$-COH_{(S)} + H^{+} \longrightarrow -COH_{2}^{+}(S)$$
 (4)

where the subscript(s) designates the coal surface. Such reactions have also been reported for carbon surface oxygen functionality (8-10).

Figure 2 shows the quantities of calcium adsorbed by the lignite as a function of pH. It is observed that calcium uptake is not only inhibited in strongly acidic media (pH < 4), but calcium is actually extracted from the coal into solution, as indicated by the negative calcium values. However, calcium adsorption progressively increased as the pH's of the coal slurries increase. These trends are consistent with the surface charge properties of the coals. As the coal particles become more negatively charged, coal-ca²⁺ interactions become more pronounced as a result of electrostatic interaction between the metal ions (Ca²⁺) and the anionic coal surface. A similar trend was obtained for potassium adsorption onto the coals.

In synopsis, for the first time, it has been shown from the current study that coal surface charge exerts a predominant influence on the adsorption of coal gasification metal ions from solution. Metal ion adsorption is favored in highly alkaline solution, while it is suppressed in strongly acidic environments. Thus, efficient catalyst impregnation and improved catalyst dispersion and activity may be obtained by controlling the pH and the surface charge on coals.

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Table 1. Properties of Coals Used

Penn State Sample Number Seam	PS0C-1482 Hagel	PS0C-1485 Rosebud
State	N. Dakota	Montana
Rank	Lignite	Subbit. B
Ultimate Analysis (daf, %)		
Carbon	71.34	75.78
Hydrogen	4.5	5.30
Nitrogen	1.14	1.19
Total Sulfur	0.79	0.99
Oxygen (by diff.)	22.24	16.75
Proximate Analysis (As Rec'd, %)	
Moisture	34.45	25,37
Volatile Matter	28.18	27.43
Fixed Carbon	31.80	38.67
Ash	5.57	8.54

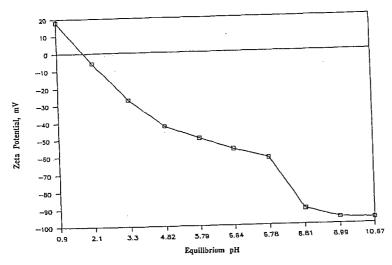


Figure 1: Dependence of Zeta Potential on pH for North Dakota (Hagel) Lignite [PSOC 1482]. Ionic strength was controlled with 10⁻³ moles 1⁻¹ AgNO₃.

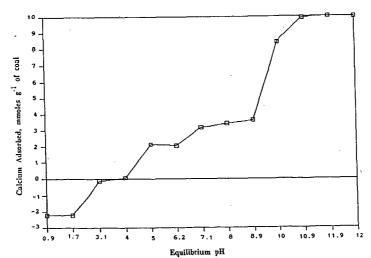


Figure 2: Calcium Adsorption as a Function of pH by Hagel Lignite (FSOC 1482).